



CERTIFICATE OF VERIFICATION

I, Sumi Kim of 15th Floor, Hibrand Building 215, Yangjae-dong, Seocho-gu, Seoul, Republic of Korea state that the English translation of Korean Patent Application No.2002-66184 is a true and complete translation to the best of my knowledge of the Korean-English language and that the writings contained in the English translation are correct English translation of the Certificate of Patent Application of the Korean patent Application No. 2002-66184.

Dated this 10th day of May,2006.

Signature of translator: _____

Sumi KIM

KOREAN INTELLECTUAL PROPERTY OFFICE

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【Purport】 According to the Korean Patent law 42 and 60, I, hereby,

file the patent application and request for examination.

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ABSTRACT

The present invention provides a composition for preparing porous interlayer dielectric thin film, said
5 composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving said two solid components. There is also provided a dielectric thin film having evenly distributed nano-pores with a diameter less
10 than 50Å, which is required for semiconductor devices.

REPRESENTATIVE DRAWING

Fig.1

15 INDEX

Nano-pores, monomeric saccharide, oligomeric saccharide, porogen, low dielectric thin film , interlayer dielectric film for semiconductor

SPECIFICATION

TITLE OF INVENTION

COMPOSITION FOR PREPARING POROUS DIELECTRIC THIN FILM
CONTAINING SACCHARIDES POROGEN

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a pore size distribution of thin film prepared in Example 6-3.

Fig. 2 is a graph showing a pore size distribution of
10 thin film prepared in Example 6-4.

DETAILED DESCRIPTION

OBJECT OF THE INVENTION

FIELD OF THE INVENTION AND BACKGROUND OF THE RELATED ART

15 The present invention relates to a composition for preparing porous interlayer dielectric thin film containing saccharides porogen. More specifically, the present invention relates to a composition comprising saccharide derivatives as porogen, capable of forming nano-pores with
20 a diameter less than 50Å and a process for preparing porous semiconductor interlayer dielectric thin film in semiconductor device.

Substances having nano-pores have been known to be useful for absorbents, carriers for catalysts, thermal
25 insulators and electric insulators in various fields. In

particular, they have been recently reported useful as materials for insulating films between interconnect layers in semiconductor devices. As the integration level has been increased in semiconductor devices, the performance of the devices is determined by the speed of wires. Accordingly, the storage capacity of interconnect thin film is required to be lowered to decrease the resistance and capacity in wires. For this purpose, there have been attempts to use materials with low dielectric constant in the insulating film. For example, US Patent Nos. 3,615,272, 4,399,266 and 4,999,397 disclose polysilsesquioxanes with a dielectric constant of 2.5~3.1 which can be used in Spin On Deposition(SOD), as an alternative for SiO₂ with a dielectric constant of 4.0 which has been used in Chemical Vapor Deposition(CVD). In addition, US Patent No. 5,965,679 describes organic high molecules with a dielectric constant of 2.65~2.70, polyphenylenes. However, the dielectric constants of the previous matrix materials are not sufficiently low to achieve a very low dielectric constant less than 2.50 required for high-speed devices.

To solve this problem, there have been various trials to incorporate air bubbles into these organic and inorganic matrixes at a nano-scale. In this connection, US Patent No. 6,231,989 B1 describes a method to form a porous thin film by the treat of the ammonia through the mixing of high

boiling point solvent, which can form pores on the hydrogen silsesquioxane. Further, US Patent Nos. 6,114,458, 6,107,357 and 6,093,636 disclose a method for preparing very low dielectric constant substances comprising the
5 steps of: vinyl-based high molecular dendrimer porogen which is degradable in the heating step in the same method with that disclosed in US Patent No. 6,114,458; and mixing the dendrimer porogen with organic or inorganic matrix; making a thin film using the mixture; and decomposing the
10 porogens contained in the mixture at a high temperature to form nano-pores.

However, the porous substances produced by such methods have a problem that their pore sizes are as large as 50~100Å in diameter and distribution thereof is ununiform.

15

FEATURE OF THE INVENTION

A feature of the present invention is to provide a composition for preparing dielectric thin film wherein a number of pores with a diameter less than 50Å are uniformly
20 distributed.

Another feature of the present invention is to provide a method for forming dielectric thin film between interconnect layers in semiconductor devices, which have a dielectric constant k of 2.5 or less, by using said
25 composition.

In accordance with one aspect of the present invention, there is provided a composition for preparing substances having porous interlayer dielectric thin film, said composition comprising a saccharide or saccharide derivative; a thermo-stable organic or inorganic matrix precursor; and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

In accordance with another aspect of the present invention, there is provided a method for forming dielectric thin films between interconnect layers in semiconductor devices, said method comprising: coating the said composition on a substrate; evaporating the solvent therefrom; and heating the coating film at 150~600°C under inert gas atmosphere or vacuum condition.

In accordance with still another aspect of the present invention, there is provided a substance having nano-pores, said substance being prepared by using the composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be explained in more detail in the following Examples with reference to the

accompanying drawings

According to the present invention, there is provided novel substances having evenly distributed nano-pores with a diameter less than 50Å, wherein said substances are made from a composition comprising thermo-stable organic or inorganic matrix precursors and thermo-unstable saccharide derivatives. These substances can be applied to a range of uses, including absorbent, carriers for catalysts, thermal insulators, electric insulators, and low dielectrics. In particular, these substances can be used to form thin films having very low dielectric constant as insulating films between interconnect layers in semiconductor devices.

The thermo-stable matrix precursors used in the composition of the present invention may be organic or inorganic high molecules having a glass transition temperature higher than 400°C.

Examples of these inorganic high molecule include, without limitation, (1)silsesquioxane, (2)alkoxy silane sol with a number average molecular weight of 500~20,000 derived from partial condensation of SiOR_4 , RSiOR_3 or R_2SiOR_2 (R is organic substituents), (3)a polysiloxane with a number average molecular weight of 1000~1000,000 derived from partial condensation of more than one kind of cyclic or cage structure-siloxane monomer selectively mixing with more than one kind of silane based-monomer such as Si(OR)_4 ,

Rsi(OR)_3 or $\text{R}_2\text{Si(OR)}_2$ (R is organic substituents).

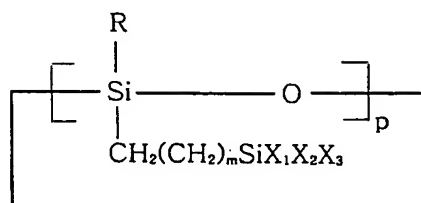
Particularly, the silsesquioxane can be exemplified by hydrogen silsesquioxane, alkyl silsesquioxane, aryl silsesquioxane, and copolymer of these silsesquioxanes.

5 In addition, organic high molecules, which cure into stable reticular structure at a high temperature, are also preferred as the matrix precursor. Non-limiting examples of the organic high molecule include polyimide-based polymers, which can be imidized, such as poly (amic acid),
10 poly (amic acid ester), etc.; polybenzocyclobutene-based polymers; and polyarylene-based polymers such as polyphenylene, poly (arylene ether), etc.

In the present invention, the matrix precursor is more preferably an organic polysiloxane, having Si-OH content of
15 at least 10mol%, preferably 25mol% or more, which is prepared through hydrolysis and polycondensation of at least one siloxane monomer having cyclic or cage structure by using acidic catalyst and water in the presence of a solvent, selectively mixing with at least one silane
20 monomer such as Si(OR)_4 , Rsi(OR)_3 or $\text{R}_2\text{Si(OR)}_2$ (R is organic substituents). The mole ratio of siloxane monomer having either cyclic or cage structure to the silane monomer is 0.99:0.01 ~ 0.01:0.99, more preferably 0.8:0.2 ~ 0.1:0.9, preferably 0.6:0.4 ~ 0.2:0.8 range.

25 The siloxane monomer having cyclic structure can be

represented by the following formula (1):



(1)

In the above formula (1),

R is hydrogen atom, C₁₋₃ alkyl group, C₃₋₁₀ cycloalkyl group, or C₆₋₁₅ aryl group;

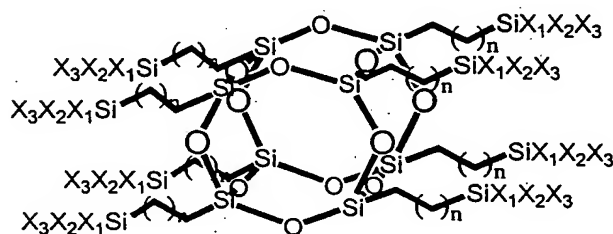
X₁, X₂ and X₃ are independently C₁₋₃ alkyl group, C₁₋₁₀ alkoxy group, or halogen atom, and at least one of them is a hydrolysable group;

p is an integer ranging from 3 to 8; and

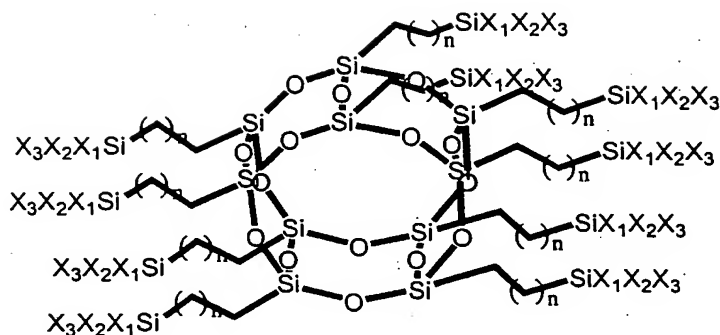
m is an integer ranging from 0 to 10.

The method for preparing the cyclic siloxane monomers is not specifically limited, but hydrosililation using a metal catalyst is preferred.

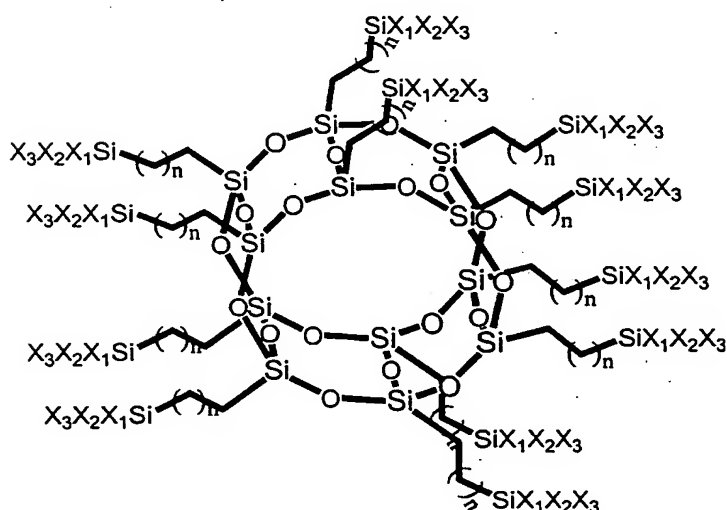
The siloxane monomers having cage structure can be represented by the following formulas (2) to (4):



(2)



(3)



(4)

In the above formulas (2) to (4),

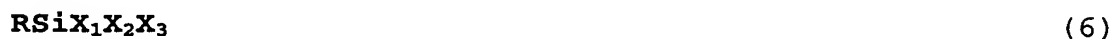
X_1 , X_2 and X_3 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of them is hydrolysable; and

n is an integer ranging from 1 to 12.

As can be seen from the above formulas (2) to (4), silicon atoms are linked to each other through oxygen atoms to form cyclic structure, and the end of each branch comprises organic groups constituting a hydrolysable substituent.

The method of preparing siloxane monomers having cage structure is not specially limited, but hydrosilation using metallic catalyst is preferred.

5 The silane-based monomers can be represented by the following formulas (5) to (7):



10



In the above formulas (5) to (7),

R₁ and R₂ are respectively hydrogen atom, C₁₋₃ alkyl group, C₃₋₁₀ cycloalkyl group, or C₆₋₁₅ aryl group; and

15 X₁, X₂, X₃ and X₄ are independently C₁₋₃ alkyl group, C₁₋₁₀ alkoxy group, or halogen atom.

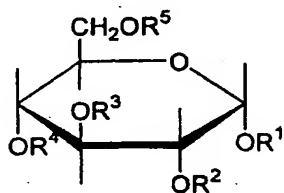
The catalyst used in the condensation reaction for preparing matrix monomers is not specifically limited, but preferably hydrochloric acid, benzenesulfonic acid, oxalic
20 acid, formic acid, or mixtures thereof.

In the hydrolysis and polycondensation reaction, water is added at 1.0~100.0 equivalents, preferably 1.0~10.0 equivalents per one equivalent of reactive groups in the monomers, and the catalyst is added at 0.00001~10
25 equivalents, preferably 0.0001~5 equivalents per one

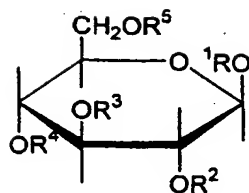
equivalent of reactive groups in the monomers, and then the reaction is carried out at 0~200°C, preferably 50~110°C for 1~100hrs, preferably 5~24hrs. In addition, the organic solvent used in this reaction is preferably aromatic hydrocarbon solvent such as toluene, xylene, mesitylene, acetone, etc.; ketone-based solvent such as methyl isobutyl ketone, acetone, etc.; ether-based solvent such as tetrahydrofuran, isopropyl ether, etc.; acetate-based solvent such as propylene glycol monomethyl ether acetate; amide-based solvent such as dimethylacetamide, dimethylformamide, etc.; γ-butyrolactone; silicon solvent; or a mixture thereof.

The thermo-unstable porogens used in the present invention are monomeric, dimeric, a polymeric saccharide or a derivative thereof comprising of 1~22 of hexacarbon saccharides.

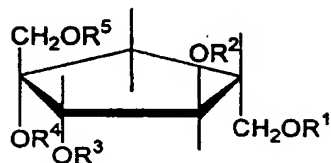
Concrete examples are monosaccharides such as glucose derivatives represented by the following formula (8), galactose derivatives represented by the following formula (9), fructose derivatives representative by the following formula (10):



(8)



(9)

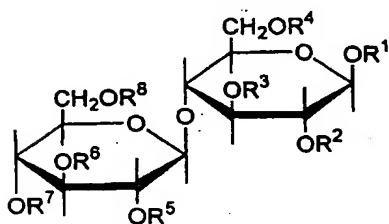


(10)

In the above formulas (8) to (10),

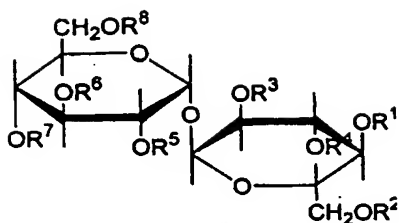
5 R_1 , R_2 , R_3 , R_4 and R_5 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group.

Another examples of the porogen used in the present invention is disaccharides such as lactose derivatives
10 represented by the following formula (11), maltose derivatives represented by the following formula (12), disaccharide-based sucrose derivatives represented by the following formula (13).

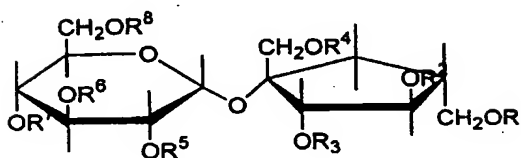


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(11)



(12)

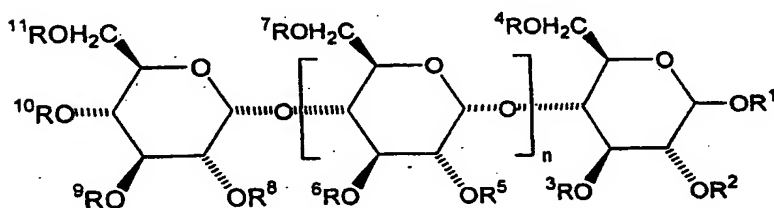


(13)

In the above formulas (11) to (13),

- 5 $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ and R_8 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, C_{1-20} carboxy alkyl group.

Yet another examples of the porogen used in the present
 10 invention is polysaccharide represented by the following formula (14).



(14)

In the above formula (14),

- 15 $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}$ and R_{11} are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl

group, C₃₋₁₀ cycloalkyl group, C₆₋₃₀ aryl group, C₁₋₂₀ hydroxy alkyl group, or C₁₋₂₀ carboxyl group and n is an integer ranging from 1 to 20.

Specific examples of the porogen include, but not
5 limited to, glucose, glucopyranose pentabenzoate, glucose pentaacetate, galactose, galactose pentaacetate, fructose, sucrose, sucrose octabenzoate, sucrose octaacetate, maltose, lactose, etc.

In the present invention, the composition for producing
10 substances having nano-pores may be prepared by dissolving the above mentioned thermo-stable matrix precursors and the thermo-unstable cyclodextrin-based porogens in an appropriate solvent. Examples of this solvent include, but not limited to, aromatic hydrocarbons such as anisole,
15 mesitylene and xylene; ketones such as methyl isobutyl ketone, 1-methyl-2-pyrrolidinone and acetone; ethers such as tetrahydrofuran and isopropyl ether; acetates such as ethyl acetate, butyl acetate and propylene glycol methyl ether acetate; amides such as dimethylacetamide and
20 dimethylformamide; γ -butyrolactone; silicon solvents; and mixtures thereof.

The solvent should be used in sufficient amount to coat
a substrate fully with the two solid components (matrix precursor + cyclodextrin derivative), and may be present in
25 the range of 20~99.9 wt.% in the composition, preferably

50~95 wt.%. If the solvent is used less than 20 wt.%, there is a problem that a thin film is not formed evenly due to high viscosity. To the contrary, if the solvent is used more than 99.9 wt.%, the thickness of the film is too thin.

5 The content of the saccharide is preferably 0.1~95 wt.%, more preferably 10~70 wt.% of the solid components (matrix precursor + porogen). If the porogen is used more than 70 wt.% there is a problem that a thin film is not used interlayer insulator because the mechanical property of the
10 film is lowered. To the contrary, if the porogen is used less than 10wt.%, the dielectric constant of the film is not lowered due to the lowered generation of pores.

According to the present invention, the thin film having nano-pores is formed on a substrate by the use of
15 the composition of the present invention, and serves as a good interlayer insulating film required for semiconductor devices. The composition of the present invention is first coated onto a substrate through spin-coating, dip-coating, spray-coating, flow-coating, screen-printing and
20 so on. More preferably, the coating step is carried out by spin-coating at 1000~5000 rpm. Following the coating, the solvent is evaporated from the substrate for a resinous film to deposit on the substrate. At this time, the evaporation may be carried out by simple air-drying, or by
25 subjecting the substrate, at the beginning of curing step,

to vacuum condition or mild heating ($\leq 100^{\circ}\text{C}$). The resulting resinous coating film may be cured by heating at a temperature of $150\sim 600^{\circ}\text{C}$, more preferably $200\sim 450^{\circ}\text{C}$ wherein pyrolysis of the cyclodextrin-based porogen occurs, so as to provide insoluble film without crack. As used herein, by "film without crack" is meant a film without any crack observed with an optical microscope at a magnification of 1000X. As used herein, by "insoluble film" is meant a film, which is substantially insoluble in any solvent described as being useful for the coating and deposition of the siloxane-based resin. The heat-curing of the coating film may be performed under inert gas (nitrogen, argon, etc.) atmosphere or vacuum condition for even 10hrs, preferably 30min to 2hrs.

After the curing, fine pores with a diameter less than 50\AA is formed in the matrix. More fine pores with a diameter less than 30\AA may be evenly formed, for example, through chemical modification of saccharide porogen.

The thin film obtained from the above has a low dielectric constant ($k \leq 2.5$). Further, in the case that 30 weight parts of the saccharide porogen are mixed with 70 weight parts of the matrix precursor (i.e., content of the cyclodextrin derivative is 30wt.% of the solid mixture), very low dielectric constant ($k \leq 2.2$) may be also achieved.

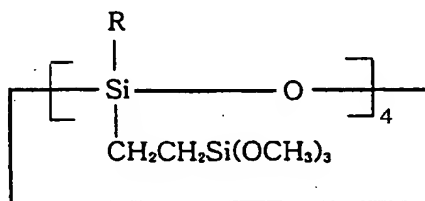
Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are given for the purpose of illustration and are not to be construed as limiting the scope of the invention.

Example 1 - Synthesis of matrix monomers

Example 1-1: Synthesis of matrix monomer A

To a flask were added 29.014mmol(10.0g) of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane and 0.164g of platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex(solution in xylene), and then diluted with 300ml diethylether. Next, the flask was cooled to -78°C, 127.66mmol(17.29g) trichlorosilane was slowly added thereto, and then the flask was slowly warmed to room temperature. The reaction was continued at room temperature for 20hrs, and any volatile materials were removed from the reaction mixture under reduced pressure of about 0.1torr. To the mixture was added 100ml pentane and stirred for 1hr, and then the mixture was filtered through celite to provide a clear colorless solution. The pentane was evaporated from the solution under reduced pressure of about 0.1torr to afford a colorless liquid compound, $[-\text{Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{SiCl}_3)\text{O}]_4$ in a yield of 95%. 11.28mmol(10.0g) of the compound was diluted with 500ml tetrahydrofuran, and

136.71mmol(13.83g) triethylamine was added thereto. Thereafter, the mixture was cooled to -78°C , 136.71mmol(4.38g) methyl alcohol was slowly added thereto, and it was slowly warmed again to room temperature. The reaction was continued at room temperature for 15hrs followed by filtration of the product mixture through celite, and then volatile materials were evaporated from the filtrate under reduced pressure of about 0.1torr. Subsequently, 100ml pentane was added thereto and stirred for 1hr, and then the mixture was filtered through celite to provide a clear colorless solution. The pentane was evaporated from this solution under reduced pressure of about 0.1torr to afford monomer A represented by the following formula (15) as a colorless liquid in a yield of 94%:



(15)

Example 2 - Synthesis of matrix precursors

Example 2-1 Precursor A : Homopolymerization of monomer A

To a flask was added 9.85mmol(8.218g) monomer A, and

then diluted with 90ml tetrahydrofuran. Next, dil. HCl solution (1.18mmol hydrochloride) prepared by mixing of 8.8ml conc. HCl (35wt.% hydrochloride) with 100ml D.I.-water was slowly added thereto at -78°C , followed by
5 addition of more D.I.-water, so that total amount of water including the inherent water in the above added dil. HCl solution might be 393.61mmol(7.084g). Thereafter, the flask was slowly warmed to 70°C , and allowed to react for 16hrs. Then, the reaction mixture was transferred to a
10 separatory funnel, 90ml diethylether was added thereto, and then rinsed with 100ml D.I.-water 5times. Subsequently, 5g anhydrous sodium sulfate was added thereto and stirred at room temperature for 10hrs to remove a trace of water, and then filtered out to provide a clear colorless solution.
15 Any volatile materials were evaporated from this solution under reduced pressure of about 0.1torr to afford 5.3g of precursor A as white powder.

Example 2-2

20 **Precursor B: Copolymerization of monomer A and methyltrimethoxysilane**

To a flask were added 37.86mmol(5.158g) methyltrimethoxysilane and 3.79mmol(3.162g) monomer A, and then diluted with 100ml tetrahydrofuran. Next, dil. HCl
25 solution (0.0159mmol hydrochloride) prepared by dilution of

0.12ml conc. HCl (35wt.% hydrochloride) with 100ml D.I.-
water was slowly added thereto at -78°C , followed by
addition of more D.I.-water, so that total amount of water
including the inherent water in the above added dil. HCl
5 solution may be 529.67mmol(9.534g). Thereafter, the flask
was slowly warmed to 70°C , and allowed to react for 16hrs.
Then, the reaction mixture was transferred to a separatory
funnel, 100ml diethylether was added thereto, and then
rinsed with 100ml D.I.-water five times. Subsequently, 5g
10 anhydrous sodium sulfate was added thereto and stirred at
room temperature for 10hrs to remove a trace of water, and
then filtered out to provide a clear colorless solution.
Any volatile materials were evaporated from this solution
under reduced pressure of about 0.1torr to afford 5.5g of
15 precursor B as white powder.

Example 2-3

Precursor C: Copolymerization of monomer A and tetramethoxy silane

20 To a flask were added 13.28mmol(11.08g) monomer A and
2.39mmol(2.00g) tetramethoxy silane, and then diluted with
100ml tetrahydrofuran. Next, dil. HCl solution (0.0159mmol
hydrochloride) prepared by dilution of 0.12ml conc. HCl
(35wt.% hydrochloride) with 100ml D.I.-water was slowly
25 added thereto at -78°C , followed by addition of more D.I.-

water, so that total amount of water including the inherent water in the above added dil. HCl solution may be 529.67mmol(9.534g). Thereafter, the flask was warmed to 70° C, and allowed to react for 16hrs. Then, the reaction mixture was transferred to a separatory funnel 100ml diethylether was added thereto, and then rinsed with 100ml D.I.-water five times. Subsequently, 5g of anhydrous sodium sulfate was added thereto and stirred at room temperature for 10hrs to remove a trace of water, and then filtered out to provide a clear colorless solution. Any volatile materials were evaporated from this solution under reduced pressure of about 0.1torr to afford 6.15g of precursor C as white powder.

Example 3: Analysis of the prepared precursors

The siloxane-based resinous precursors thus prepared were analyzed for weight average molecular weight (hereinafter, referred to as "MW") and molecular weight distribution (hereinafter, referred to as "MWD") by means of gel permeation chromatography (Waters Co.), and the Si-OH, Si-OCH₃ and Si-CH₃ contents (mol%) of their terminal groups were analyzed by means of NMR analysis(Bruker Co.). The results are set forth in the following Table 1.

Table 1

Precursor	MW	MWD	Si-OH (%)	Si-OCH ₃ (%)	Si-CH ₃ (%)
Precursor (A)	60800	6.14	35.0	1.2	63.8
Precursor (B)	4020	2.77	39.8	0.5	59.7
Precursor (C)	63418	6.13	26.3	0.7	73.0

$$\text{Si-OH (mol\%)} = \frac{\text{Area (Si-OH)}}{[\text{Area (Si-OH)} + 3\text{Area (Si-OCH}_3\text{)} + 3\text{Area (Si-CH}_3\text{)}]} \times 100$$

$$\text{Si-OCH}_3 \text{ (mol\%)} = \frac{3\text{Area (Si-OCH}_3\text{)}}{[\text{Area (Si-OH)} + 3\text{Area (Si-OCH}_3\text{)} + 3\text{Area (Si-CH}_3\text{)}]} \times 100$$

$$5 \quad \text{Si-CH}_3 \text{ (mol\%)} = \frac{3\text{Area (Si-CH}_3\text{)}}{[\text{Area (Si-OH)} + 3\text{Area (Si-OCH}_3\text{)} + 3\text{Area (Si-CH}_3\text{)}]} \times 100$$

Example 4: Determination of thickness and refractive index of the thin film made from the substance having nano-pores

The resinous compositions of the present invention were prepared by mixing the siloxane-based resinous matrix precursor obtained from the above Example 2 together with saccharide based-porogen and propylene glycol methyl ether acetate (PGMEA) in accordance with the particular ratios as described in the following Table 2. These compositions were applied to spin-coating at 3000rpm onto p-type silicon wafers doped with boron. The substrates thus coated were then subjected to a series of soft baking on a hot plate for 1min at 150°C and another min at 250°C, so that the organic solvent might be sufficiently removed. Then, the

substrates were cured in a Linberg furnace at 420°C for 60mins under vacuum condition. Thereafter, the thickness of each resulting low dielectric film was determined by using prism coupler and the refractive index determined by using 5 prism coupler and ellipsometer. The results are set forth in the following Table 2.

Table 2.

Example	Matrix precursor	Porogen	Mat. ⁽¹⁾ (wt.%)	CD ⁽²⁾ (wt.%)	Thickness (Å)	Dielectric constant (k)
Example 4-1	Precursor A	Not added	25.0	—	8245	1.437
Example 4-2	Precursor A	Sucrose octabenzoate	25.0	30	8637	1.328
Example 4-3	Precursor B	Not added	30.0	—	10424	1.414
Example 4-4	Precursor B	Sucrose octabenzoate	30.0	30	11764	1.304
Example 4-5	Precursor C	Not added	25.0	—	11340	1.440
Example 4-6	Precursor C	Glucose pentaacetate	25.0	35	10247	1.418
Example 4-7	Precursor C	Sucrose octaacetate	25.0	35	13942	1.318
Example 4-8	Precursor C	Sucrose octabenzoate	25.0	35	8578	1.298

Mat.⁽¹⁾ (wt.%) = [weight of matrix precursor(g)+weight of
porogen(g)] / [weight of PGMEA(g)+weight of precursor(g) +
weight of porogen(g)] x 100

CD⁽²⁾ (wt.%) = weight of porogen(g) / [weight of porogen(g)
5 +weight of matrix precursor(g)] x 100

**Example 5: Preparing determiner of dielectric constant
of the thin film and determination of dielectric constant
of the thin film**

10 To determine the dielectric constant of the porous thin
film , 3000Å thickness silicon thermo oxide film were
applied onto p-type silicon wafers doped with boron, then
100Å titanium , 2000Å aluminum were deposited by metal
evaporator. Subsequently, low dielectric films in
15 composition of Table 3 were coated as example 4. Thereafter,
1mm diameter circular aluminum thin film is deposited at
2000Å thickness by the hard mask designed to have 1mm
electrode diameter to complete [MIM(Metal- insulator-
metal)]-dielectric constant determiner in [MIM(Metal-
20 insulator-metal)] structure. Capacitance of these thin
films was measured by PRECISION LCR METER(HP4284A) with
Probe station(Micromanipulator 6200 probe station), at
100Hz frequency. The thickness of thin film measured by a
prism coupler is substituted into following equation, to
25 provide the electric constant.

$$k = (C \times d) / (\epsilon_0 \times A)$$

k : dielectric constant

C : capacitance

5 d : the thickness of the low dielectric thin film

ϵ_0 : dielectric constant in vacuum

A : the contact area of electrode

Table 3

Example	Matrix precursor	Porogen	Mat. (wt.%)	CD (wt.%)	Pore Content ⁽¹⁾ (%)	Dielectric constant (k)
Example 5-1	Precursor B	Not added	25.0	—	—	2.75
Example 5-2	Precursor B	Sucrose octabenzoate	25.0	10	4.1	2.52
Example 5-3	Precursor B	Sucrose octabenzoate	25.0	20	10.9	2.19
Example 5-4	Precursor B	Sucrose octabenzoate	25.0	30	20.5	2.01
Example 5-5	Precursor C	Not added	25.0	—	—	2.92
Example 5-6	Precursor C	Glucose pentaacetate	25.0	35	3.9	2.82
Example 5-7	Precursor C	Sucrose octaacetate	25.0	35	10.7	2.56
Example 5-8	Precursor C	Sucrose octabenzoate	25.0	35	27.0	1.94

10 Pore Content⁽¹⁾ (%) = calculated from the refraction index

measured by using prism coupler, by Lorentz-Lorentz equation

Example 6: Measuring of the average size and size distribution of the pores in the prepared porous thin film

Nitrogen adsorption analysis with Surface Area Analyzer[ASAP2010, Micromeritics co.] was performed to analyze the pore structure of the thin films prepared by the same process as in Example 4 in the composition of following Table 4. Thin film has very small average size less than 20Å as described in Table 4. Fig.1 and Fig 2 describe pore size distributions of the thin film prepared in Examples 6-3 and 6-4.

15

Table 4

Example	Matrix precursor	Porogen	Mat. (wt.%)	CD (wt.%)	Average pore size(Å)	Volume of pore (cc/g)	Surface area (m ² /g)
Example 6-1	Precursor C	Not added	25.0	—	6.1	0.008	164
Example 6-2	Precursor C	Glucose pentaacetate	25.0	30.0	16.2	0.166	412
Example 6-3	Precursor C	Sucrose octabenzoate	25.0	30.0	14.6	0.451	631
Example 6-4	Precursor C	Sucrose octabenzoate	25.0	30.0	16.3	0.455	681

UTILITY OF THE INVENTION

The present invention provide a composition for preparing dielectric thin film wherein a number of pores with a diameter less than 50\AA are uniformly distributed.

- 5 Hence, the composition of the present invention can be applied to a range of uses, including absorbent, carriers for catalysts, thermal insulators, electric insulators, and low dielectrics, in particular dielectric thin film between interconnect layers in semiconductor devices, which have a
- 10 dielectric constant k of 2.5 or less.

WHAT IS CLAIMED IS:

1. A composition for preparing substances having porous interlayer dielectric thin film, said composition
5 comprising:

a saccharide or saccharide derivative;

a thermo-stable organic or inorganic matrix precursor; and

a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

10

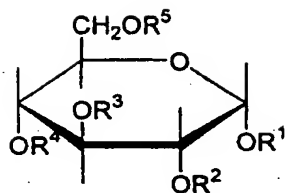
2. The composition according to claim 1, wherein the content of the saccharide or saccharide derivative is 0.1~95 wt.% of the solid components(the matrix precursor + the saccharide or saccharide derivative).

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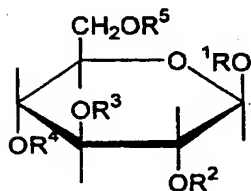
3. The composition according to claim 1, wherein the content of the solvent is 20.0~99.9 wt.% of the compositions(the matrix precursor + the saccharide or saccharide derivative + the solvent).

20

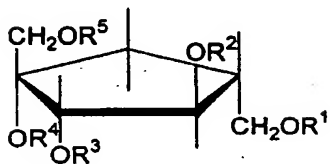
4. The composition according to claim 1, wherein the saccharide or saccharide derivative is selected from the group consisting of one or more monomeric saccharide derivatives represented by the following formulas (8) to
25 (10):



(8)



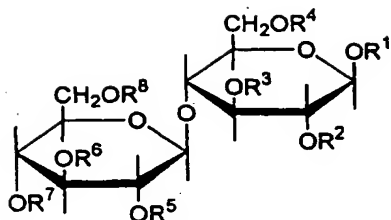
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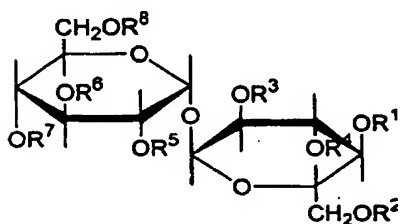
(10)

5 in which, R_1 , R_2 , R_3 , R_4 and R_5 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group.

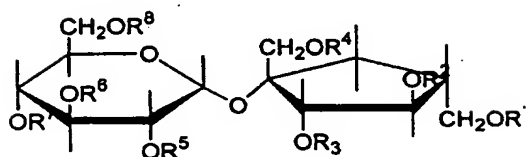
10 5. The composition according to claim 1, wherein the saccharide or saccharide derivative is selected from the group consisting of disaccharide derivatives represented by the following formulas (11) to (13):



(11)



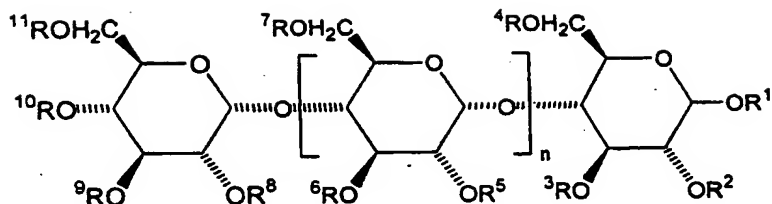
(12)



(13)

in which, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 and R_8 are independently
 5 hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10}
 cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group,
 C_{1-20} carboxy alkyl group.

6. The composition according to claim 1, wherein the
 10 saccharide or saccharide derivative is selected from the
 group consisting of polymeric saccharide derivatives
 represented by the following formula (14)



(14)

in which, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , R_{10} and R_{11} are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group and n is an integer ranging from 1 to 20.

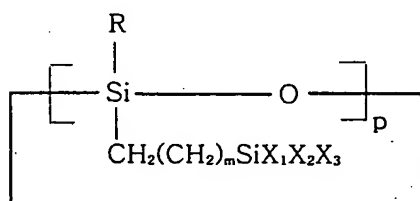
7. The composition according to claim 1, wherein the saccharide or saccharide derivative is glucose, glucopyranose pentabenzoate, glucose pentaacetate, galactose, galactose pentaacetate, fructose, sucrose, sucrose octabenzoate, sucrose octaacetate, maltose or lactose.

8. The composition according to claim 1, wherein the matrix precursor is silsesquioxane, alkoxy silane sol, or siloxane-based polymer.

9. The composition according to claim 8, wherein the silsesquioxane is hydrogen silsesquioxane, alkyl silsesquioxane, aryl silsesquioxane, or a copolymer thereof.

10. The composition according to claim 1, wherein the

matrix precursor is a siloxane-based resin which is prepared by hydrolysis and polycondensation of one or more monomers selected from the group consisting of compounds represented by the following formulas (1) to (4), using a catalyst and water in an organic solvent:



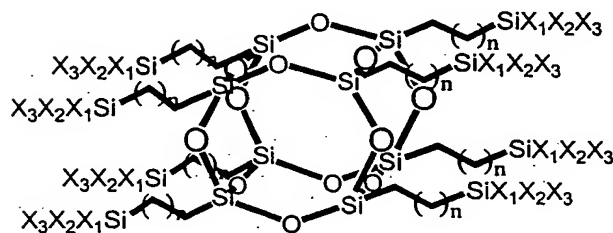
(1)

in which, R is hydrogen atom, C₁₋₃ alkyl group, C₃₋₁₀ cycloalkyl group, or C₆₋₁₅ aryl group;

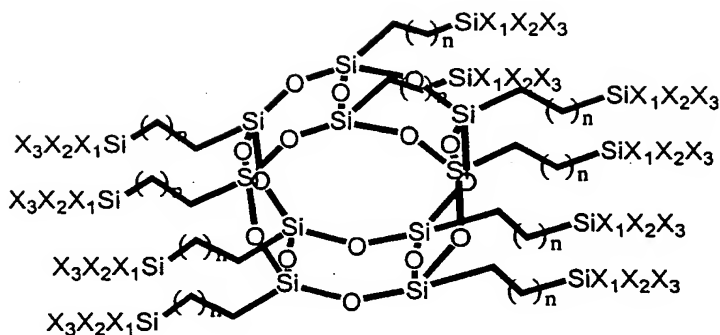
X₁, X₂ and X₃ are independently C₁₋₃ alkyl group, C₁₋₁₀ alkoxy group, or halogen atom, and at least one of them is a hydrolysable group;

p is an integer ranging from 3 to 8;

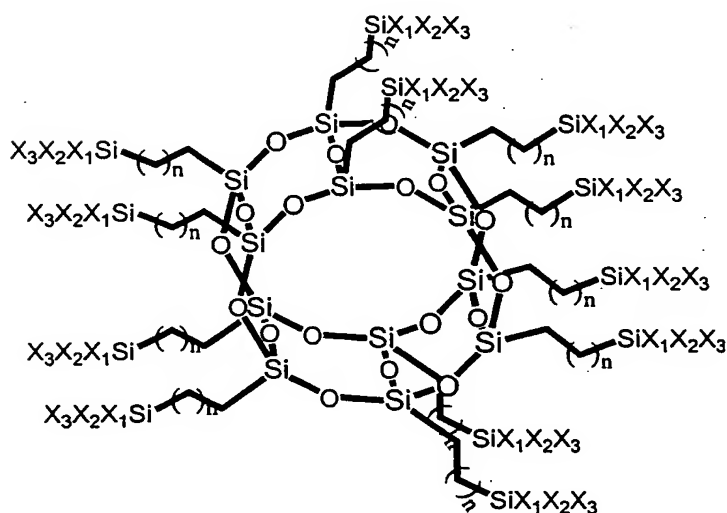
m is an integer ranging from 0 to 10; and



(2)



(3)



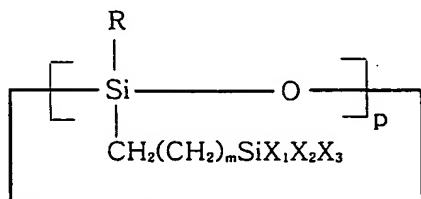
(4)

in which, X_1 , X_2 and X_3 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of
5 them is hydrolysable; and

n is an integer ranging from 1 to 12.

11. The composition according to claim 1, wherein the
matrix precursor is siloxane-based resin which is prepared
10 by hydrolysis and polycondensation of a mixture of one or
more monomers selected from the group consisting of
compounds represented by the following formulas (1) to (4)

together with one or more silane-based monomers selected from the group consisting of compounds represented by the following formulas (5) to (7) using a catalyst and water in an organic solvent:



5

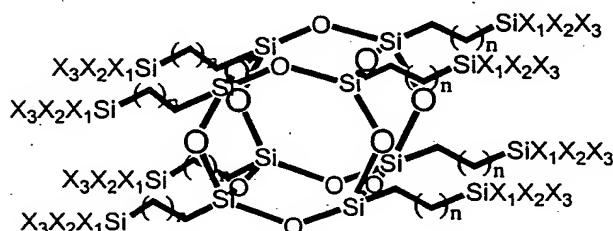
(1)

in which, R is hydrogen atom, C₁₋₃ alkyl group, C₃₋₁₀ cycloalkyl group, or C₆₋₁₅ aryl group;

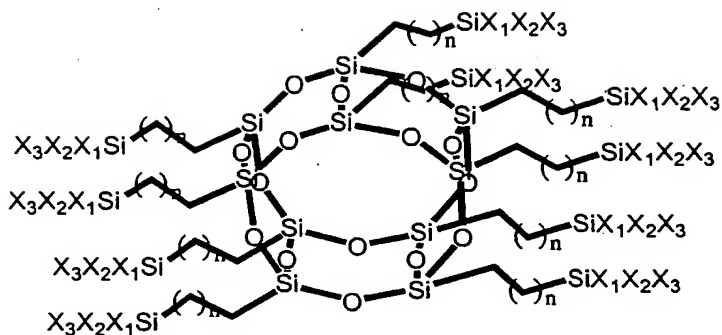
X₁, X₂ and X₃ are independently C₁₋₃ alkyl group, C₁₋₁₀ alkoxy group, or halogen atom, and at least one of them is
10 a hydrolysable group;

p is an integer ranging from 3 to 8;

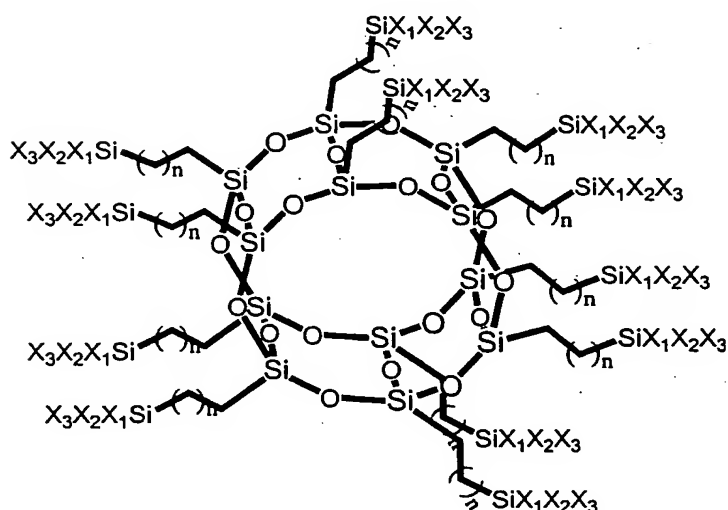
m is an integer ranging from 0 to 10; and



(2)



(3)



(4)

in which, X_1 , X_2 and X_3 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of them is hydrolysable;

n is an integer ranging from 1 to 12; and



in which, R_1 and R_2 are respectively hydrogen atom, C_{1-3} alkyl group, C_{3-10} cycloalkyl group, or C_{6-15} aryl group; and

X₁, X₂, X₃ and X₄ are independently C₁₋₃ alkyl group, C₁₋₁₀ alkoxy group, or halogen atom.

12. The composition according to claim 10 or claim 11,
5 wherein the content of the matrix precursor is more than 10 mol%.

13. The composition according to claim 11, wherein the
mole ratio of the siloxane monomers having cyclic or cage
10 structure to the silane-based monomers is
0.99:0.01~0.01:0.99.

14. The composition according to claim 1, wherein the
matrix precursor is polyimide, polybenzocyclobutene,
15 polyarylene, or a mixture thereof.

15. The composition according to claim 1, wherein the
solvent is aromatic hydrocarbon-based solvent, ketone-based
solvent, ether-based solvent, acetate-based solvent, amide-
20 based solvent, γ -butyrolactone, silicon-based solvent, or a
mixture thereof.

16. A method for forming dielectric thin films between
interconnect layers in semiconductor devices, said method
25 comprising:

coating a composition of claim 1 on a substrate;
evaporating the solvent therefrom; and
heating the coating film at 150~600°C under inert gas
atmosphere or vacuum condition.

5

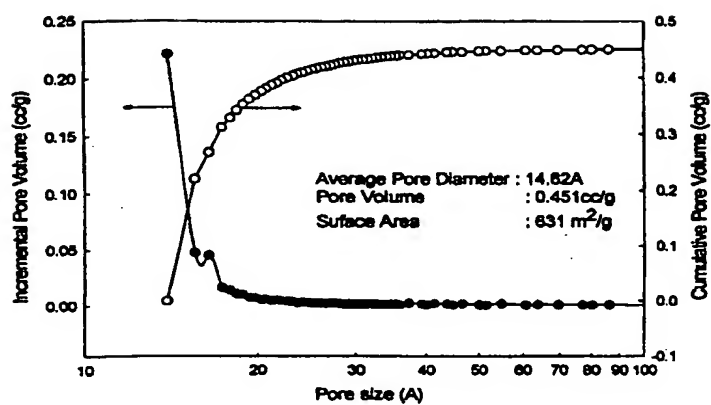
17. The method according to claim 16, wherein the
coating is carried out by spin-coating at 1000~5000rpm.

18. A substance having nano-pores, said substance being
10 prepared by using the composition of claim 1.

19. A method for applying the substance of claim 18 to
a range of uses, including absorbent, carriers for
catalysts, thermal insulators, electric insulators, and low
15 dielectrics

DRAWINGS

FIG. 1



5

FIG. 2

